



زیست حسگر نوری غیر آنزیمی گلوکز مبتنی بر نانومیله های اکسید روی رشد یافته بر روی برد مدار چاپی

محمد رضا نورگستر، زهیر کردروستی

شیراز - دانشگاه صنعتی شیراز - دانشکده مهندسی برق و الکترونیک

چکیده - زیست حسگر گلوکز فلورسانت برمبنای نانومیله های اکسید روی که بر روی زیرلایه برد مدار چاپی رشد داده شده است ساخته شده است. لایه ی بذری بر روی برد مدار چاپی به روش لایه نشانی دورانی ایجاد و نانومیله های اکسید روی بر روی زیر لایه به روش هیدروترمال رشد داده شده است. در ساخت سنسور گلوکز پیشنهاد شده، دما و مدت زمان جدید برای آنیلینگ مورد استفاده قرار گرفته است. نمودار انکسار اشعه ایکس و تصویر میکروسکوپ روبشی الکترونی نشان میدهد که نانومیله های اکسید روی طی پروسه رشد به نحو مطلوبی شکل گرفته اند. خروجی این سنسور بر اساس طیف سنجی فتولومینسانس میباشد. پس از مراحل لازم برای ساخت این بایوسنسور، پاسخ طیف فلورسانت به ازای غلظت های مختلف گلوکز اندازه گیری شده است. پاسخ ها، نشان دهنده حساسیت بالای این بیوسنسور نسبت به تغییرات غلظت های مختلف گلوکز میباشد که این میزان تغییرات برای غلظت های مختلف گلوکز مورد بحث و مقایسه قرار گرفته است.

کلید واژه - سنسور گلوکز، فتولومینسانس، نانومیله، اکسید روی، هیدروترمال

Non-Enzymatic Optical Glucose Biosensor Using Grown ZnO Nanorods on Printed Circuit Boards

Mohammadreza Nourgostar, Zoheir Kordrostami*

Department of Electrical Engineering, Shiraz University of Technology, Shiraz, Iran

m.nourgostar@sutech.ac.ir, kordrostami@sutech.ac.ir

Abstract- A fluorescent glucose biosensor based on the grown ZnO nanorods on printed circuit boards (PCBs) has been fabricated. The ZnO nanorods have been grown on the conductive PCBs using hydrothermal method. The seed layer has been spin coated on PCBs. New annealing temperatures and durations have been utilized in fabricating the proposed fluorescent glucose biosensor. XRD pattern and SEM image show that ZnO nanorods have been formed in the desired form during the growth process. The biosensor output is based on the photoluminescence (PL) spectra. After essential treatments of the sensor, 1 mM to 80 mM glucose concentrations have been drop casted on the PCBs and their PL response were measured. The results show the high sensitivity of the fabricated sensor to the glucose concentration variations. The amount of the change in PL spectra for different glucose concentrations has been quantified and discussed.

Keywords: Glucose Biosensor, ZnO Nanorods, Hydrothermal Growth, photoluminescence.

1. Introduction

Nanoscale zinc oxide (ZnO) structures have been one of the most commonly used semiconductor nanostructures due to the wide band gap energy (3.3 eV), the ability to absorb bio-materials and large excitation binding energy (60 meV) [1-3]. ZnO nanostructures have a wide range of applications such as chemical, UV, gas, PH and bio sensors. Nanostructures made from ZnO have been synthesized in different configurations like thin films, nanobelts, nanorods and nanowires as the sensing element [4, 5]. The morphology and structural properties of ZnO play an important role in its characteristics [2, 6]. Due to its low temperature and low cost, the hydrothermal method is more attractive than the other ZnO nanorod growth methods [2, 7]. Also, diverse substrates can also be used for growing ZnO nanostructures. Conductive substrates like ITO, FTO and Cu are attractive candidates [8, 9]. One of the most common applications of the ZnO is sensing glucose with nanorod arrays. Recently, enzymatic and electrochemical glucose biosensors have been studied extensively [4]. However, in this paper, we propose a non-enzymatic optical glucose biosensor. By application of the photo luminescence (PL) spectra, the change in the peaks of the PL results can be used as the response of the biosensor.

2. Experiment

2.1. Preparing the Substrate

PCBs have been used as substrate because of their low cost, high conductivity and the possibility of ZnO growth on them using hydrothermal method. We polished the PCB surfaces by fine sand paper to reach a homogenous surface. The polished PCB has been washed with DI water and sonicated in acetone, ethanol and DI water each for 10 minutes. The PCB samples were let dry in air. The spin coating of the seed layer has been shown in Fig. 1.

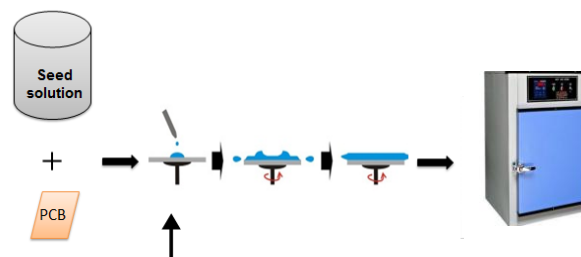


Fig. 1. Seed layer spin coating process.

2.2. The Seed Layer

We mixed 10 mM zinc acetate dehydrate in 60 ml ethanol and 30 mM NaOH in 30 ml ethanol as seed solution. The zinc solution was kept on the heater stirrer at 60 °C for 3 h to mix well and NaOH was added dropwisely to reach a milky solution. After stirring, the seed solution was cooled down to room temperature and kept for 24 h. The seed layer has been spin coated on the substrate. The spin coater speed has been set to 1500 rpm and then 2500 rpm each for 30 s. The substrates have been put in the oven at 60 °C for 10 min to dry and then the spin coating process has been repeated again for 5 times to have thicker seed layers. The PCBs have finally been placed at 95 °C to be dried completely.

2.3. Growing ZnO Nanorods

The ZnO nanorods have been grown using hydrothermal method. The solution used for growing ZnO nanorods has been composed of 25 mM zinc nitrate hexahydrate and 25 mM HMTA solved in DI water and stirred for 5 h at 50 °C. A centrifuge tube has been filled with the solution to 80% and a substrate has been put in it and put in air oven for 6h at 95 °C. The sample has been washed with DI water and then annealed at 100 °C for 1h. The process has been shown in Fig. 2.

3. Characterization

XRD has been used to analyse the formation of ZnO nanocrystals. The XRD (1.54 Å) pattern for the prepared samples has been shown in Fig. 3. The peaks confirm the wurtzite crystal structure of ZnO

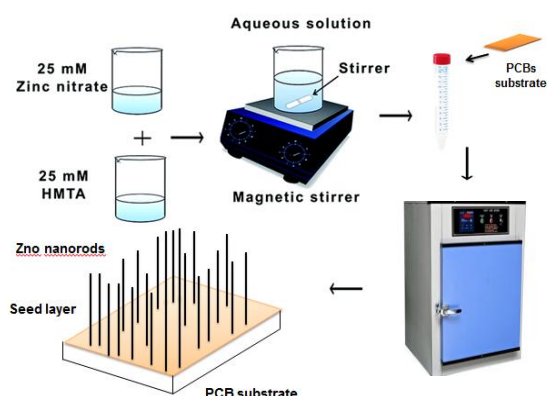


Fig. 2. The growing process of the ZnO nanorods.

nanorods along the c-axis ((002) direction). The formation of CuO as well as ZnO on the PCBs has been shown. The SEM image of the sample has been shown in Fig. 4. As shown, ZnO nanorods have been grown successfully with average diameters from 40 nm to 80 nm. The XRD and SEM, verify the formation of the ZnO nanorods with the desired characteristics.

4. Optical Response of the Biosensor

PL is a simple and beneficial method without uncertainties usually occur in cyclic voltammetry method and is considered a more improved method. Sensitivity of the sensor to the glucose has been tested using 1 mM to 80 mM β -D glucose. Photoluminescence spectroscopy (325 nm He-Cd laser) has been used to test different glucose concentrations. The sensitivity has been defined as the relative change of the peak intensities to the change in the glucose concentration. The reaction between UV irradiation

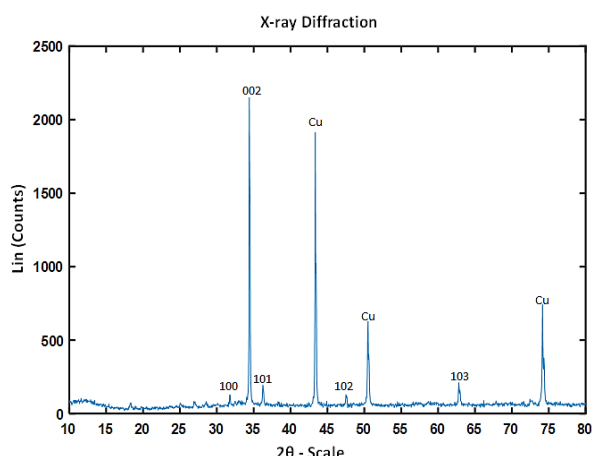


Fig. 3. XRD of grown ZnO nanorods on PCB substrate.

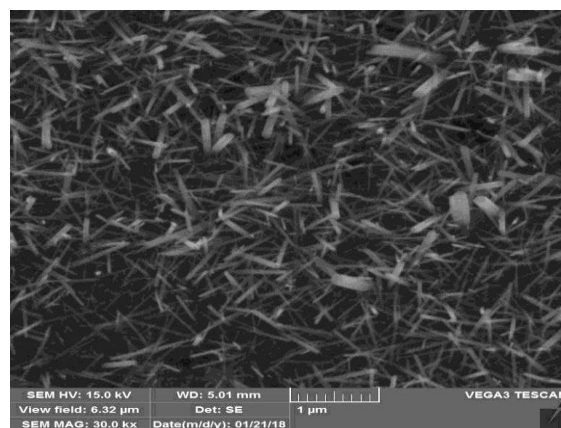


Fig. 4. The SEM image of ZnO nanorods grown on a PCB substrate.

(excited from laser) and ZnO surface plays the role of catalyst. When ZnO surface is treated with glucose and the surface is exposed to UV, free carriers are generated and accepted by the glucose solution before recombination. The products of the oxidation reaction are H_2O_2 and gluconic acid (Eq. (1)). The quenching of the PL intensity peaks by increasing the glucose concentration is due to the increase in the oxidation reaction.



We prepared 1mM, 5mM, 10mM and 80mM glucose solutions. 15 μ L of each glucose solution has been dropped on the ZnO nanorods. The results of the PL spectra have been shown in Fig. 5. As shown, the topmost graph is the result for the ZnO nanorods without glucose. Since the highest change

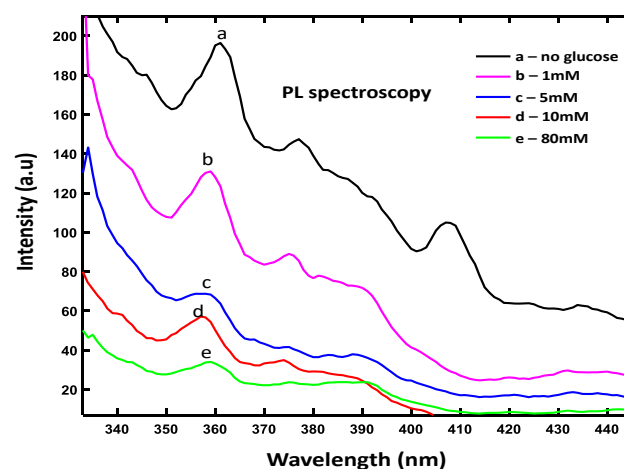


Fig. 5. PL spectra of ZnO nanorods on PCBs treated with 1mM, 5mM, 10mM and 80mM glucose solutions.

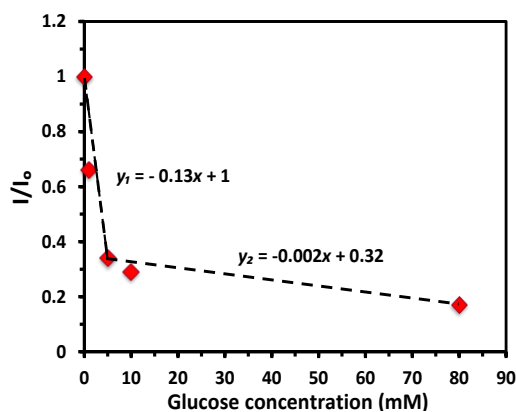


Fig. 6. Variations of the peak Intensity of PL spectra versus glucose concentration.

In the peak intensities has been occurred in the UV wavelengths about 360 nm, this wavelength has been chosen for calculating the dependence of the optical output on the glucose concentration. It has also been observed that by increasing the glucose concentration from zero to 80mM, the intensity of the peaks around 360 nm has been decreased. The intensity and the normalized intensity (I/I_0) of the peaks of the PL spectra for different glucose concentrations have been shown in Table I.

5. Biosensor Sensitivity

In Fig. 6 the peak intensities of the PL response have been plotted versus the glucose concentration. Linear interpolation has been used to estimate the sensitivity. Since the peak variations in low concentrations is much larger than that of the high concentrations we have interpolated the results in two regions separately. The slope of the lines represents the sensitivity in each region. The sensitivity has been obtained 13% and 0.2% in low and high glucose concentration regions respectively. First region with higher linear slope ranges from 0 mM to 10 mM glucose concentration. Since glucose in normal human serum ranges from 4.4 mM to 6.6 mM and higher for diabetics, the sensing range and detection sensitivity especially in the first region, are well suited.

Table I. The details of the PL results.

Glucose (mM)	0	1	5	10	80
Intensity (a.u)	196.3	131	68.32	57.14	34.03
I/I_0	1	0.66	0.34	0.29	0.17

6. Conclusion

A glucose biosensor based on the semiconducting ZnO nanostructures was fabricated. The hydrothermal method with new annealing temperatures and durations was used to grow ZnO nanorods. Cheap conductive PCBs was used as substrates on which the seed layer was spin coated. XRD and SEM characterizations verified the formation of ZnO nanorods. The sensor output was analysed based on the variations in the peaks intensities of the PL spectra for different glucose concentrations. The results showed that for low concentrations of glucose the biosensor has a very good sensitivity which is much better than that of higher glucose concentrations.

References

- [1] S. Baruah, M. Jaisai, R. Imani, M. M. Nazhad, and J. Dutta, "Photocatalytic paper using zinc oxide nanorods," *Science and technology of advanced materials*, vol. 11, no. 5, p. 055002, 2010.
- [2] S. Öztürk, N. Kılınc, N. Taşaltın, and Z. Z. Öztürk, "Fabrication of ZnO nanowires and nanorods," *Physica E: Low-Dimensional Systems and Nanostructures*, vol. 44, no. 6, pp. 1062-1065, 2012.
- [3] A. Khayatian, V. Asgari, A. Ramazani, S. Akhtarianfar, M. A. Kashi, and S. Safa, "Diameter-controlled synthesis of ZnO nanorods on Fe-doped ZnO seed layer and enhanced photodetection performance," *Materials Research Bulletin*, vol. 94, pp. 77-84, 2017.
- [4] A. Rodrigues, M. Castegnaro, J. Arguello, M. Alves, and J. Morais, "Development and surface characterization of a glucose biosensor based on a nanocolumnar ZnO film," *Applied Surface Science*, vol. 402, pp. 136-141, 2017.
- [5] P. Van Thanh, H. H. Mai, N. V. Tuyen, S. C. Doanh, and N. C. Viet, "Zinc Oxide Nanorods Grown on Printed Circuit Board for Extended-Gate Field-Effect Transistor pH Sensor," *Journal of Electronic Materials*, vol. 46, no. 6, pp. 3732-3737, 2017.
- [6] S. Rackauskas *et al.*, "A novel method for continuous synthesis of ZnO tetrapods," *The Journal of Physical Chemistry C*, vol. 119, no. 28, pp. 16366-16373, 2015.
- [7] K.-X. Zhang *et al.*, "Synthesis, structural and optical properties of silver nanoparticles uniformly decorated ZnO nanowires," *Chemical Physics Letters*, vol. 698, pp. 147-151, 2018.
- [8] J. Fan, T. Li, and H. Heng, "Hydrothermal growth of ZnO microrods on ITO-coated glass substrate," *Applied Physics A*, vol. 119, no. 1, pp. 185-192, 2015.
- [9] K. Gautam, I. Singh, P. Bhatnagar, and K. R. Peta, "The effect of growth temperature of seed layer on the structural and optical properties of ZnO nanorods," *Superlattices and Microstructures*, vol. 93, pp. 101-108, 2016.